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TITLE OF THE INVENTION (280 characters max)			
THE USE OF SULFUR CONTAINING INITIATORS FOR ANIONIC POLYMERIZATION OF MONOMERS			
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Cynthia M. Wilson Sec'y to Donald J. Bobak

P01090US1A (P313)

EL726086572US

THE USE OF SULFUR CONTAINING INITIATORS FOR ANIONIC POLYMERIZATION OF MONOMERS

BACKGROUND OF THE INVENTION

5 Anionic polymerization is a well-known type of chain-reaction polymerization that typically employs either a base or an organometallic as a polymerization initiator. Exemplary organometallics that are well-known as anionic-polymerization initiators for diene monomers, with and without monovinyl aromatic monomers, include alkyllithium, trialkyltin lithium, and certain aminolithium
10 compounds. The synthesis of lithiodithiane reagents is known as is their addition to conjugated ketones. However, no use of sulfur containing initiators, particularly lithio thio acetals based compounds, is known for anionic polymerization.

 Anionic polymerization of diene monomers such as butadiene and isoprene, with and without monovinyl aromatics such as styrene, commonly yields
15 elastomers that can be used in a variety of commercial applications; one such application involves employing the elastomers in constructing tires. Because of the great commercial demand for these types of elastomers, there is a need for anionic-polymerization initiators that can be employed for their synthesis.

 Synthesis of a polymer having a head group that will interact with the
20 filler, used to reinforce many elastomeric compounds, and thereby reduce hysteresis is desirable.

SUMMARY OF THE INVENTION

 In general, the present invention advances the art by providing a new
25 organometallic anionic polymerization initiator for polymerizing diene monomers.

 The present invention provides a method for anionically polymerizing monomers comprising the step of polymerizing the monomers with a sulfur containing anionic initiator to provide a functional head group on the polymer.

 The present invention further provides a method for synthesizing a
30 polymer comprising a headgroup functionality that can reduce the hysteresis of an elastomeric compound comprising both the polymer and a filler material.

Additionally, anionically polymerizing monomers, using lithio thio acetals as an initiator, yields polymers comprising a bis-alkyl sulfide headgroup functionality that can react with fillers such as carbon black and silica.

5 The present invention further provides vulcanizable elastomeric compounds having a bis-alkyl sulfide head group functionality that is reactable with reinforcing fillers having phenolic functionalities, thereby providing reduced hysteresis.

10 The present invention also provides pneumatic tires having at least one component manufactured from a vulcanizable elastomeric compound having a bis-alkyl sulfide head group functionality that is reactable with reinforcing fillers having phenolic functionalities, thereby providing reduced hysteresis.

In general, the present invention provides a method for anionically polymerizing monomers comprising the step of polymerizing the monomers with a sulfur containing anionic initiator to provide a functional head group on the polymer.

15 The present invention also provides a method for anionically polymerizing monomers comprising the steps of synthesizing a sulfur containing anionic initiator *in situ* and polymerizing the monomers with the sulfur containing anionic initiator to provide a functional head group on the polymer.

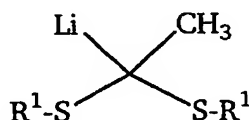
20 The present invention also provides a vulcanizable elastomer having reduced hysteresis properties comprising a plurality of polymer molecules wherein substantially each polymer molecule contains a functional head group derived from a sulfur containing anionic initiator; and from about 20 to about 100 parts by weight of carbon black, per 100 parts of the elastomer.

25 The present invention also provides an improved tire having decreased rolling resistance resulting from a treadstock containing a vulcanizable elastomer compound comprising an elastomer comprising a plurality of polymer molecules wherein substantially each polymer molecule contains a functional head group derived from a sulfur containing anionic initiator; and from about 20 to about 100 parts by weight of carbon black, per 100 parts of the elastomer.

30

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

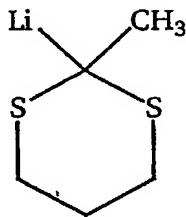
The present invention provides a method for anionically polymerizing monomers by employing lithio thio acetals as a polymerization initiator. Suitable lithio thio acetals have the general formula



where R is selected from the group consisting of trimethyl-, triethyl- and tripropyl-silyl groups, C1 to C20 alkyl groups, C4 to C20 cycloalkyl groups, C6 to C20 aryl group and mixtures thereof and where R' is selected from the group consisting of C1 to C20 alkyl groups, C4 to C20 cycloalkyl groups, C6 to C20 aryl group, C2 to C8 alkylene groups and mixtures thereof. The R and R' groups could have additional functionality such as dimethylaminopropyl, *p*-dimethylaminopropyl and *t*-amines, ethers, thioethers. A preferred initiator is 2-lithio-2-methyl-1,3-dithiane.

In particular, polymerization can be initiated by contacting 2-lithio-2-methyl-1,3-dithiane with a solution comprising diene monomer. This can be achieved by either adding the initiator to a solution comprising diene monomer, or it can be achieved by synthesizing the initiator in a solution comprising diene monomer (*in situ* 2-lithio-2-methyl-1,3-dithiane).

2-lithio-2-methyl-1,3-dithiane can be represented as follows:



As stated above, 2-lithio-2-methyl-1,3-dithiane is employed as an anionic polymerization initiator by contacting it with a solution comprising diene

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monomers. The solution is generally heated to about 24°C before the initiator is added thereto or synthesized therein. After the initiator contacts the solution, the reaction temperature is generally increased to about 54°C. Anionic polymerization of the diene monomer is generally complete after approximately 25 minutes.

5 The lithio thio acetals can be employed as an anionic polymerization initiator in amounts ranging from about 1 to about 1000 meq/kg of monomer. Preferably, they are employed in amounts ranging from about 3 to about 12 meq/kg of monomer. More preferably, the initiator is employed in an amount ranging from about 4 to about 8 meq/kg of monomer.

10 The initiator thus formed may be employed as an initiator to prepare any anionically-polymerized elastomer, e.g., polybutadiene, polyisoprene and the like, and copolymers thereof with monovinyl aromatics such as styrene, alpha methyl styrene and the like, or trienes such as myrcene. Thus, the elastomers include diene homopolymers and copolymers thereof with monovinyl aromatic polymers. Suitable monomers include
15 conjugated dienes having from about 4 to about 12 carbon atoms and monovinyl aromatic monomers having 8 to 18 carbon atoms and trienes. Examples of conjugated diene monomers and the like useful in the present invention include 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene and 1,3-hexadiene, and aromatic vinyl monomers include styrene, α -methylstyrene, *p*-methylstyrene, vinyltoluene and
20 vinyl naphthalene.

Non-limiting examples of useful polymers that can be synthesized by methods that employ 2-lithio-2-methyl-1,3-dithiane as an anionic polymerization initiator include, but are not limited to polybutadiene, styrene-butadiene rubber, synthetic polyisoprene, butadiene-isoprene rubber, styrene-isoprene rubber, styrene-
25 isoprene-butadiene rubber, and terminal and backbone functionalized derivatives thereof.

Polymerization is conducted in polar solvent, such as tetrahydrofuran (THF), or a hydrocarbon solvent, such as the various oligomers of hexanes, heptanes, octanes, pentanes, their alkylated derivatives, and mixtures thereof. In order to
30 promote randomization in copolymerization and to control vinyl content, a polar

coordinator may be added to the polymerization ingredients. Amounts range between 0 and 90 or more equivalents per equivalent of lithium. The amount depends on the amount of vinyl desired, the level of styrene employed and the temperature of the polymerization, as well as the nature of the specific polar coordinator (modifier) employed. Suitable polymerization modifiers include for example, ethers, or amines to provide the desired microstructure and randomization of the comonomer units.

Other compounds useful as polar coordinators include tetrahydrofuran (THF), linear and cyclic oligomeric oxolanyl alkanes such as 2,2-bis(2'-tetrahydrofuryl) propane, di-piperidyl ethane, di-piperidyl methane, hexamethylphosphoramide, N-N'-dimethylpiperazine, diazabicyclooctane, dimethyl ether, diethyl ether, tributylamine and the like. The linear and cyclic oligomeric oxolanyl alkane modifiers are described in U.S. Pat. No. 4,429,091, owned by the Assignee of record, the subject matter of which relating to such modifiers is incorporated herein by reference. Compounds useful as polar coordinators include those having an oxygen or nitrogen hetero-atom and a non-bonded pair of electrons. Other examples include dialkyl ethers of mono and oligo alkylene glycols; "crown" ethers; tertiary amines such as tetramethylethylene diamine (TMEDA); linear THF oligomers; and the like.

A batch polymerization is begun by charging a blend of monomer(s) and hydrocarbon solvents to a suitable reaction vessel, followed by the addition of the polar coordinator (if employed) and the initiator compound previously described. The reactants are heated to a temperature of from about 20° to about 200° C, and the polymerization is allowed to proceed for from about 0.1 to about 24 hours.

To terminate the polymerization, and thus further control polymer molecular weight, a terminating agent, coupling agent or linking agent may be employed, all of these agents being collectively referred to herein as "terminating reagents". Certain of these reagents may provide the resulting polymer with a multifunctionality. That is, the polymers initiated according to the present invention, may carry the functional head group as discussed hereinabove, and may also carry a

second functional group selected from the group consisting of terminating reagents, coupling agents and linking agents.

Useful terminating reagents are disclosed in U.S. Pat. Nos. 5,502,131, 5,496,940 and 4,616,069, the subject matters of which are incorporated herein by reference. They include the following compounds providing terminal functionality (e.g., "endcapping"): tin tetrachloride, $(R)_3SnCl$, $(R)_2SnCl_2$, $RSnCl_3$, carbodiimides, N-cyclic amides, N,N' disubstituted cyclic ureas, cyclic amides, cyclic ureas, isocyanates, Schiff bases, 4,4'-bis(diethylamino) benzophenone, and the like. Tin tetrachloride is preferred. The organic moiety R is selected from the group consisting of alkyls having from about 1 to about 20 carbon atoms, cycloalkyls having from about 3 to about 20 carbon atoms, aryls having from about 6 to about 20 carbon atoms and aralkyls having from about 7 to about 20 carbon atoms. Typical alkyls include n-butyl, s-butyl, methyl, ethyl, isopropyl and the like. The cycloalkyls include cyclohexyl, menthyl and the like. The aryl and the aralkyl groups include phenyl, benzyl and the like. Preferred endcapping agents are selected from the group consisting of tin tetrachloride, tributyl tin chloride, dibutyl tin dichloride and 1,3-dimethyl-2-imidazolidinone.

While terminating to provide a functional group on the terminal end of the polymer is preferred, it is further preferred to terminate by a coupling reaction, with for example, tin tetrachloride or other coupling agent such as silicon tetrachloride ($SiCl_4$), esters and the like.

2-lithio-2-methyl-1,3-dithiane is a well-known composition that can be synthesized by persons having ordinary skill in the art by using conventional techniques. A non-limiting example of a method for preparing 2-lithio-2-methyl-1,3-dithiane involves adding 2-methyl-1,3-dithiane to dried tetrahydrofuran and cooling to $-78^\circ C$. A solution comprising butyllithium and hexane is then added thereto. The resulting solution is then stirred for approximately 3 hours and allowed to stand overnight at $-25^\circ C$.

In an alternate embodiment, 2-lithio-2-methyl-1,3-dithiane can be synthesized *in situ* in a solution comprising the monomer or monomers to be

polymerized. A non-limiting example for performing this synthesis involves creating a solution comprising hexane, styrene monomer, and butadiene. This first solution is generally heated to about 24°C when 2-methyl-1,3-dithiane and butyllithium are added thereto. The solution is then heated to approximately 54°C and allowed to react for approximately 40 minutes. More generally, the *in situ* preparation of anionic initiator is practiced by creating a solution comprising hexane, and the monomer(s) to be polymerized. This first solution is generally heated to about 24°C when the non-lithiated initiator precursor and butyllithium are added thereto. The solution is then heated to approximately 54°C and allowed to react for approximately 40 minutes, or comparable conditions necessary to allow the precursor and butyllithium to react.

The anionic polymers produced herein have functional headgroups, derived from the initiators of the present invention, which interact with conventional fillers used in the formulation of vulcanizable elastomeric (rubber) compounds. Typically, such fillers include silica or carbon black. The polymers can be compounded with silica in amounts ranging from about 5 to about 100 parts by weight, per 100 parts of rubber (phr), with about 10 to about 90 phr being preferred.

The polymers can be compounded with carbon black in amounts ranging from about 20 to about 100 parts by weight, per 100 parts of rubber (phr), with about 40 to about 70 phr being preferred. The carbon blacks may include any of the commonly available, commercially-produced carbon blacks but those having a surface area (EMSA) of at least 20 m²/g and more preferably at least 35 m²/g up to 200 m²/g or higher are preferred. Surface area values used in this application are those determined by ASTM test D-1765 using the cetyltrimethyl-ammonium bromide (CTAB) technique. Among the useful carbon blacks are furnace black, channel blacks and lamp blacks. More specifically, examples of the carbon blacks include super abrasion furnace (SAF) blacks, high abrasion furnace (HAF) blacks, fast extrusion furnace (FEF) blacks, fine furnace (FF) blacks, intermediate super abrasion furnace (ISAF) blacks, semi-reinforcing furnace (SRF) blacks, medium processing channel blacks, hard processing channel blacks and conducting channel blacks. Other carbon blacks which may be utilized include acetylene blacks. Mixtures of two or more of the above blacks can be used in preparing the carbon

black products of the invention. Typical values for surface areas of usable carbon blacks are summarized in the following Table I.

TABLE I
Carbon Blacks

5	ASTM Designation (D-1765-82a)	Surface Area (m ² /g) (D-3765)
10	N-110	126
	N-220	111
	N-339	95
	N-330	83
	N-550	42
15	N-660	35

The carbon blacks utilized in the preparation of the rubber compounds of the invention may be in pelletized form or an unpelletized flocculant mass. Preferably, for more uniform mixing, unpelletized carbon black is preferred. The reinforced rubber compounds can be cured in a conventional manner with known vulcanizing agents at about 0.5 to about 4 phr. For example, sulfur or peroxide-based curing systems may be employed. For a general disclosure of suitable vulcanizing agents one can refer to Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed., Wiley Interscience, N.Y. 1982, Vol. 20, pp. 365-468, particularly "Vulcanization Agents and Auxiliary Materials" pp. 390-402. Vulcanizing agents may be used alone or in combination.

Vulcanizable elastomeric compositions of the invention can be prepared by compounding or mixing the polymers thereof with carbon black and other conventional rubber additives such as fillers, plasticizers, antioxidants, curing agents and the like, using standard rubber mixing equipment and procedures and conventional amounts of such additives. Such elastomeric compounds when vulcanized using conventional rubber

vulcanization conditions have reduced hysteresis properties and are particularly adapted for use as tread rubbers for tires having reduced rolling resistance.

General Experimental

In order to demonstrate practice of the present invention, the following examples have been prepared and tested. The examples should not, however, be viewed as limiting the scope of the invention. The claims will serve to define the invention.

EXAMPLES

Example No. 1

Synthesis of 2-lithio-2-methyl-1,3-dithiane

To a 1 L N₂ purged bottle equipped with a serum cap was added 350 mL of dried tetrahydrofuran and 10 mL of 2-methyl-1,3-dithiane (83.5 mmol). The bottle was cooled to -78°C and 55.83 mL of 1.510 M butyllithium (84.3 mmol) in hexane was added. The reaction was stirred at -78°C for 3 hours and then stored at -25°C overnight. Titration of the resulting solution indicated that the solution contained 0.234M active lithium compound. To elucidate the structure of this compound, the solution was added to a dried solution of 8.26 mL of 1-bromo-3-chloropropane (83.5 mmol) in 90 mL tetrahydrofuran at -78°C. After 3 hours, the products were examined by GC/MS and found to contain >95% 2-(3-chloropropyl)-2-methyl-1,3-dithiane. No 1-chloroheptane was observed indicating that the butyllithium had completely reacted with the 2-methyl-1,3-dithiane.

Example No. 2

Synthesis of Poly(styrene-co-butadiene) with 2-lithio-2-methyl-1,3-dithiane

To a 1.75 L N₂ purged reactor equipped with a stirrer was added 1.12 kg of hexane, 0.48 kg of 33 wt% styrene in hexane, and 2.89 kg of 22.0 wt% butadiene in hexane. The reactor was then heated to 24°C and 0.5 mL of 1.6 M of a cyclic

oligomeric oxolanyl alkane modifier, according to U.S. Pat. No. 4,429,091, referenced hereinabove, in hexane and 22.63 mL of 0.234 M 2-lithio-2-methyl-1,3-dithiane in tetrahydrofuran was charged to the reactor. The reactor jacket was then heated to 54°C. After 15 minutes, the batch temperature peaked at 76.5°C. After an additional 25 minutes, the cement was removed from the reactor, coagulated in isopropanol containing butylated hydroxy toluene (BHT), and drum dried to yield a polymer with the following properties: $M_n=153$ kg/mol, $M_w=167$ kg/mol, $T_g= -44.4^\circ\text{C}$, 21.7% styrene, 1.3% block styrene, 32.1% vinyl, and 46.2% 1,4 butadiene incorporation.

10

Example No. 3

Synthesis of Poly(styrene-co-butadiene) with 2-lithio-2-methyl-1,3-dithiane

To a 1.75 L N_2 purged reactor equipped with a stirrer was added 1.12 kg of hexane, 0.48 kg of 33 wt% styrene in hexane, and 2.89 kg of 22.0 wt% butadiene in hexane. The reactor was then heated to 24°C and 0.5 mL of 1.6 M of cyclic oligomeric oxolanyl alkane modifier in hexane and 16.96 mL of 0.234 M 2-lithio-2-methyl-1,3-dithiane in tetrahydrofuran was charged to the reactor. The reactor jacket was then heated to 54°C. After 17 minutes, the batch temperature peaked at 75.7°C. After an additional 10 minutes, the cement was removed from the reactor, coagulated in isopropanol containing butylated hydroxy toluene (BHT), and drum dried to yield a polymer with the following properties: $M_n=208$ kg/mol, $M_w=240$ kg/mol, $T_g= -43.8$ -3.8°C, 22.2% styrene, 1.6% block styrene, 31.2% vinyl, and 46.5% 1,4 butadiene incorporation.

Example No. 4

Synthesis of Poly(styrene-co-butadiene) with *in situ* 2-lithio-2-methyl-1,3-dithiane

To a 1.75 L N_2 purged reactor equipped with a stirrer was added 1.07 kg of hexane, 0.48 kg of 33 wt% styrene in hexane, and 2.95 kg of 21.6 wt% butadiene in hexane. The reactor was then heated to 24°C and 0.5 mL of 1.6 M of cyclic

oligomeric oxolanyl alkane modifier in hexane and 8.47 mL of 0.5 M 2-methyl-1,3-dithiane in hexane, and 3.42 mL of 1.55 M butyllithium in hexanes was charged to the reactor. The reactor jacket was then heated to 54°C. After 28 minutes, the batch temperature peaked at 68.6°C. After an additional 10 minutes, the cement was removed from the reactor, coagulated in isopropanol containing butylated hydroxy toluene (BHT), and drum dried to yield a polymer with the following properties: $M_n=135$ kg/mol, $M_w=142$ kg/mol, $T_g=-56.6^\circ\text{C}$.

Comparative Example No. 5

10 Synthesis of Poly(styrene-co-butadiene) with butyllithium

To a 1.75 L N_2 purged reactor equipped with a stirrer was added 1.07 kg of hexane, 0.48 kg of 33 wt% styrene in hexane, and 2.95 kg of 21.6 wt% butadiene in hexane. The reactor was then heated to 24°C and 0.5 mL of 1.6 M of cyclic oligomeric oxolanyl alkane modifier in hexane and 22.6 mL tetrahydrofuran and 3.42 mL 1.55 M butyllithium in hexane was charged to the reactor. The reactor jacket was then heated to 54°C. After 15 minutes, the batch temperature peaked at 71.2°C. After an additional 10 minutes, the cement was removed from the reactor, coagulated in isopropanol containing butylated hydroxy toluene (BHT), and drum dried to yield a polymer with the following properties: $M_n=157$ kg/mol, $M_w=168$ kg/mol, $T_g=-42.5^\circ\text{C}$, 21.3% styrene, 1.1% block styrene, 33.8% vinyl, and 45.0% 1,4 butadiene incorporation.

Comparative Example No. 6

25 Synthesis of Poly(styrene-co-butadiene) with butyllithium

To a 1.75 L N_2 purged equipped with a stirrer was added 1.07 kg of hexane, 0.48 kg of 33 wt% styrene in hexane, and 2.95 kg of 21.6 wt% butadiene in hexane. The reactor was then heated to 24°C and 0.5 mL of 1.6 M of cyclic oligomeric oxolanyl alkane modifier in hexane and 16.96 mL tetrahydrofuran and 2.56 mL 1.55 M butyllithium in hexane was charged to the reactor. The reactor jacket was then

heated to 54°C. After 17 minutes, the batch temperature peaked at 75.5°C. After an additional 10 minutes, the cement was removed from the reactor, coagulated in isopropanol containing butylated hydroxy toluene (BHT), and drum dried to yield a polymer with the following properties: $M_n=190$ kg/mol, $M_w=207$ kg/mol, $T_g=-44.0^\circ\text{C}$, 22.1% styrene, 1.3% block styrene, 32.1% vinyl, and 45.9% 1,4 butadiene incorporation.

Next, three polybutadiene examples were prepared, Nos. 7-9, using butyllithium (control), 2-lithio-2-methyl-1,3-dithiane and 2-lithio-2-trimethylsilyl-1,3-dithiane, both prepared *in situ*, as initiators.

Example No. 7

Synthesis of Control polybutadiene initiated by butyllithium

To a 0.8 L nitrogen purged bottle equipped with a serum cap was added 0.47 mL of 1.6M butyl lithium in hexane. Then, 27.3 g of hexane and 272.7 g of 22.0% butadiene in hexane were added. The reaction was heated to 50° C for 4 hours. The resulting polymer solution was coagulated in isopropanol containing butylated hydroxy toluene (BHT), and drum dried to yield a polymer with the following properties: $M_n = 88.2$ kg/mol, M_w 104.5 kg/mol, Polydispersity = 1.18, $T_g = -94.2^\circ\text{C}$.

Example No. 8

Synthesis of polybutadiene initiated by *in situ* generated 2-lithio-2-methyl-1,3-dithiane

To a 0.8 L nitrogen purged bottle equipped with a serum cap was added 0.59 mL of 0.5M 2-methyl-1,3-dithiane and 0.47 mL of 1.6M butyl lithium in hexane. Then, 27.3 g of hexane and 272.7 g of 22.0% butadiene in hexane were added. The reaction was heated to 50°C for 4 hours. The resulting polymer solution was coagulated in isopropanol containing BHT, and drum dried to yield a polymer with the following properties: $M_n = 101.6$ kg/mol, M_w 127.5 kg/mol, polydispersity = 1.26, $T_g = -94.6^\circ\text{C}$.

Example No. 9**Synthesis of polybutadiene initiated by *in situ* generated 2-lithio-2-trimethylsilyl-1,3-dithiane**

5 To a 0.8 L nitrogen purged bottle equipped with a serum cap was added
0.29 mL of 1.0M 2-trimethylsilyl-1,3-dithiane and 0.47 mL of 1.6M butyl lithium in
hexane. Then, 27.3 g of hexane and 272.7 g of 22.0% butadiene in hexane were
added. The reaction was heated to 50°C for 4 hours. The resulting polymer solution
was coagulated in isopropanol containing BHT and drum dried to yield a polymer
10 with the following properties: $M_n = 81.9$ kg/mol, M_w 125.9 kg/mol, polydispersity =
1.54, $T_g = -93.9^\circ\text{C}$.

The three polybutadiene polymers were subsequently compounded with
components to prepare vulcanizable elastomeric compounds. Component parts by
weight, per 100 parts of rubber (phr) are set forth in Table II.

15

TABLE II
Vulcanizable Elastomeric Compounds

	MASTERBATCH		
	Example 10	Example 11	Example 12
Example 7	100	0	0
Example 8	0	100	0
Example 9	0	0	100
Carbon Black	50	50	50
Wax and Aromatic Oil	11.5	11.5	11.5
Stearic Acid	2	2	2
Antioxidant	1	1	1
Total	164.5	164.5	164.5

	Final Mix		
	Example 10	Example 11	Example 12
Initial	164.5	164.5	164.5
Accelerators	1.2	1.2	1.2
Zinc Oxide	2	2	2
Sulfur	1.3	1.3	1.3

- 5 The masterbatches were prepared by mixing the initial compounds in a 300 g Banbury mixer operating at 60 rpm and 133°C. First, the polymer (of Examples 7, 8 and 9, respectively) was placed in the mixer, and after 0.5 minutes, the remaining ingredients except the stearic acid were added. The stearic acid was then added after 3 minutes. The initial components were mixed for 5-6 minutes. At the end of mixing
- 10 the temperature was approximately 165°C. Each sample was transferred to a mill operating at a temperature of 60°C, where it was sheeted and subsequently cooled to room temperature.

The final components were mixed by adding the masterbatch and the curative materials to the mixer simultaneously. The initial mixer temperature was 65°C and it was operating at 60 rpm. The final material was removed from the mixer after 2.25 minutes when the material temperature was between 100 to 105°C. The
 5 finals were sheeted into Dynastat buttons and 6x6x0.075 inch (15x15x0.1875 cm) sheets. The samples were cured at 171°C for 15 minutes in standard molds placed in a hot press.

The elastomeric compounds of Example Nos. 10-12 were then subjected to physical testing, the results of which are reported in Table III.

10

TABLE III

Physical Properties of Compounded Stocks

Property	Example 10	Example 11	Example 12
MH	0.73	1.02	1.09
ML	15.92	17.54	15.8
TS 2	1.38	1.24	1.27
200% Modulus @23°C (MPa)	2.73	2.81	2.66
T _b @23°C (MPa)	11.89	14.42	13.95
E _b @23°C (%)	593.7	617.7	628.5
tan δ 7% E, 65°	0.234	0.188	0.195
ΔG' (50°C) (MPa)	2.1200	1.7460	1.6800

$$* \Delta G' = G' (@0.25\% E) - G' (@14.5\%E)$$

The data in Table III establishes a reduced tan δ (improved hysteresis) for
 15 the elastomeric compounds containing polymers carrying functional headgroup from the initiator (Examples 11 and 12) compared to the control compound (Example 10) containing the polymer of Example No. 7. Note that both tan δ and ΔG' are lower than the control, Example 10, indicating that dithiane functionalized polymers react with the fillers. The lower tan δ and ΔG' values also indicate that tires made with such
 20 rubber should have lower rolling resistance properties.

Based upon the foregoing disclosure, it should now be apparent that the use of the anionic polymerization initiators described herein provides a useful method for the polymerization of diene monomers. It is, therefore, to be understood that any variations evident fall within the scope of the claimed invention and thus, the selection of specific component elements can be determined without departing from the spirit of the invention herein disclosed and described. In particular, anionic polymerization initiators according to the present invention are not necessarily limited to those dithianes exemplified herein.

Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be duly limited to the illustrative embodiments set forth hereinabove. Thus, the scope of the invention shall include all modifications and variations that may fall within the scope of the attached claims.

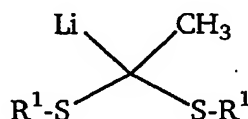
CLAIMS

What is claimed is:

1. A method for anionically polymerizing monomers comprising the step of:
 5 polymerizing said monomers with a sulfur containing anionic initiator to provide a functional head group on the polymer.

2. The method of claim 1, wherein said sulfur containing anionic initiator is a lithio thio acetal having the general formula

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where R is selected from the group consisting of trimethyl-, triethyl- and tripropyl-silyl groups, C1 to C20 alkyl groups, C4 to C20 cycloalkyl groups, C6 to C20 aryl group and mixtures thereof and where R' is selected from the group consisting of C1 to C20 alkyl groups, C4 to C20 cycloalkyl groups, C6 to C20 aryl group, C2 to C8 alkylene groups and mixtures thereof.

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3. The method of claim 2, wherein said lithio thio acetal initiator is 2-lithio-2-methyl-1,3-dithiane.

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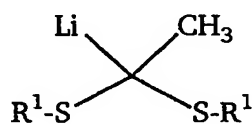
4. The method of claim 1, wherein said monomers are selected from the group consisting of conjugated dienes having from about 4 to about 12 carbon atoms and monovinyl aromatic monomers having 8 to 18 carbon atoms and trienes and mixtures thereof.

5. The method of claim 4, wherein said monomers are selected from the group consisting of styrene, butadiene, and isoprene.

6. The method of claim 1, wherein said step of polymerizing comprising the steps of:
 - providing a reaction medium;
 - adding said monomer or monomers to be polymerized to said reaction medium; and
 - adding said anionic initiator to said reaction medium.
7. The method of claim 6, wherein said reaction medium is a liquid selected from the group consisting of polar solvents, hydrocarbon solvents and mixtures thereof.
8. The method of claim 6, wherein said anionic initiator is added to said reaction medium in amounts ranging from 1 about 1000 meq/kg of said monomer.
9. The method of claim 1, further comprising the step of:
 - terminating said step of polymerizing with an agent selected from the group consisting of terminating agents, coupling agents, and linking agents to provide a functional group at the end opposite said head group.
10. The method of claim 9, wherein said terminating agents are selected from the group consisting of tin tetrachloride, $(R)_3SnCl$, $(R)_2SnCl_2$, $RSnCl_3$, carbodiimides, N-cyclic amides, N,N' disubstituted cyclic ureas, cyclic amides, cyclic ureas, isocyanates, Schiff bases, 4,4'-bis(diethylamino) benzophenone, and mixtures thereof wherein R is selected from the group consisting of alkyls having from about 1 to about 20 carbon atoms, cycloalkyls having from about 3 to about 20 carbon atoms, aryls having from about 6 to about 20 carbon atoms and aralkyls having from about 7 to about 20 carbon atoms.

11. A method for anionically polymerizing monomers comprising the steps of:
 synthesizing a sulfur containing anionic initiator *in situ*;
 polymerizing said monomers with said sulfur containing anionic
 5 initiator to provide a functional head group on the polymer.

12. The method of claim 11, wherein said sulfur containing anionic initiator is a
 lithio thio acetal having the general formula



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where R is selected from the group consisting of trimethyl-, triethyl- and
 tripropyl-silyl groups, C1 to C20 alkyl groups, C4 to C20 cycloalkyl groups, C6
 to C20 aryl group and mixtures thereof and where R' is selected from the
 15 group consisting of C1 to C20 alkyl groups, C4 to C20 cycloalkyl groups, C6 to
 C20 aryl group, C2 to C8 alkylene groups and mixtures thereof.

13. The method of claim 12, wherein said lithio thio acetal initiator is 2-lithio-2-
 methyl-1,3-dithiane.

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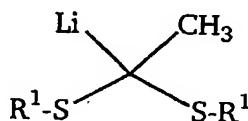
14. The method of claim 13, wherein said monomers are selected from the group
 consisting of conjugated dienes having from about 4 to about 12 carbon atoms
 and monovinyl aromatic monomers having 8 to 18 carbon atoms and trienes and
 mixtures thereof.

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15. The method of claim 14, wherein said monomers are selected from the group
 consisting of styrene, butadiene, and isoprene.

16. The method of claim 11, wherein said step of synthesizing comprises
creating a solution of an initiator precursor and butyllithium in a solvent
therefor;
adding to said solution said monomer or monomers; and
5 heating said solution for a period of time sufficient to generate said
anionic initiator.
17. The method of claim 16, wherein said initiator precursor is 2-methyl-1,3-
dithiane and said anionic initiator is 2-lithio-2-methyl-1,3-dithiane.
- 10 18. The method of claim 11, wherein said step of polymerizing comprising the
steps of:
providing a reaction medium;
adding said monomer or monomers to be polymerized to said reaction
15 medium; and
adding said anionic initiator to said reaction medium.
19. The method of claim 18, wherein said reaction medium is a liquid selected
from the group consisting of polar solvents, hydrocarbon solvents and mixtures
20 thereof.
20. The method of claim 18, wherein said anionic initiator is added to said reaction
medium in amounts ranging from 1 about 1000 meq/kg of said monomer.
- 25 21. The method of claim 11, further comprising the step of:
terminating said step of polymerizing with an agent selected from the
group consisting of terminating agents, coupling agents, and linking agents to
provide a functional group at the end opposite said head group.

22. The method of claim 21, wherein said terminating agents are selected from the group consisting of tin tetrachloride, $(R)_3SnCl$, $(R)_2SnCl_2$, $RSnCl_3$, carbodiimides, N-cyclic amides, N,N' disubstituted cyclic ureas, cyclic amides, cyclic ureas, isocyanates, Schiff bases, 4,4'-bis(diethylamino) benzophenone, and mixtures thereof wherein R is selected from the group consisting of alkyls having from about 1 to about 20 carbon atoms, cycloalkyls having from about 3 to about 20 carbon atoms, aryls having from about 6 to about 20 carbon atoms and aralkyls having from about 7 to about 20 carbon atoms.
23. A vulcanizable elastomer having reduced hysteresis properties comprising:
 a plurality of polymer molecules wherein substantially each said polymer molecule contains a functional head group derived from a sulfur containing anionic initiator; and
 from about 20 to about 100 parts by weight of carbon black, per 100 parts of said elastomer.
24. A vulcanizable elastomer according to claim 23, wherein said sulfur containing anionic initiator is a lithio thio acetal having the general formula



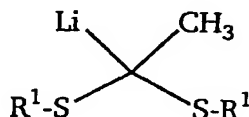
where R is selected from the group consisting of trimethyl-, triethyl- and tripropyl-silyl groups, C1 to C20 alkyl groups, C4 to C20 cycloalkyl groups, C6 to C20 aryl group and mixtures thereof and where R' is selected from the group consisting of C1 to C20 alkyl groups, C4 to C20 cycloalkyl groups, C6 to C20 aryl group, C2 to C8 alkylene groups and mixtures thereof.

25. A vulcanizable elastomer according to claim 24, wherein said lithio thio acetal initiator is 2-lithio-2-methyl-1,3-dithiane.

26. A vulcanizable elastomer according to claim 23, wherein said polymer molecules are derived from monomers selected from the group consisting of conjugated dienes having from about 4 to about 12 carbon atoms and monovinyl aromatic monomers having 8 to 18 carbon atoms and trienes and mixtures thereof.
27. A vulcanizable elastomer according to claim 26, wherein said monomers are selected from the group consisting of styrene, butadiene, and isoprene.
28. A vulcanizable elastomer according to claim 23, wherein substantially each said polymer molecule contains a functional terminal group derived from an agent selected from the group consisting of terminating agents, coupling agents, and linking agents.
29. A vulcanizable elastomer according to 28, wherein said terminating agents are selected from the group consisting of tin tetrachloride, $(R)_3SnCl$, $(R)_2SnCl_2$, R_3SnCl , carbodiimides, N-cyclic amides, N,N' disubstituted cyclic ureas, cyclic amides, cyclic ureas, isocyanates, Schiff bases, 4,4'-bis(diethylamino) benzophenone, and mixtures thereof wherein R is selected from the group consisting of alkyls having from about 1 to about 20 carbon atoms, cycloalkyls having from about 3 to about 20 carbon atoms, aryls having from about 6 to about 20 carbon atoms and aralkyls having from about 7 to about 20 carbon atoms.
30. An improved tire having decreased rolling resistance resulting from a treadstock containing a vulcanizable elastomer compound comprising:
an elastomer comprising a plurality of polymer molecules wherein substantially each said polymer molecule contains a functional head group derived from a sulfur containing anionic initiator; and

from about 20 to about 100 parts by weight of carbon black, per 100 parts of said elastomer.

31. An improved tire according to claim 30, wherein said sulfur containing anionic initiator is a lithio thio acetal having the general formula



where R is selected from the group consisting of trimethyl-, triethyl- and tripropyl-silyl groups, C1 to C20 alkyl groups, C4 to C20 cycloalkyl groups, C6 to C20 aryl group and mixtures thereof and where R' is selected from the group consisting of C1 to C20 alkyl groups, C4 to C20 cycloalkyl groups, C6 to C20 aryl group, C2 to C8 alkylene groups and mixtures thereof.

32. An improved tire according to claim 31, wherein said lithio thio acetal initiator is 2-lithio-2-methyl-1,3-dithiane.
33. An improved tire according to claim 30, wherein said polymer molecules are derived from monomers selected from the group consisting of conjugated dienes having from about 4 to about 12 carbon atoms and monovinyl aromatic monomers having 8 to 18 carbon atoms and trienes and mixtures thereof.
34. An improved tire according to claim 33, wherein said monomers are selected from the group consisting of styrene, butadiene, and isoprene.
35. An improved tire according to claim 30, wherein substantially each said polymer molecule contains a functional terminal group derived from an agent selected from the group consisting of terminating agents, coupling agents, and linking agents.

36. An improved tire according to 35, wherein said terminating agents are selected from the group consisting of tin tetrachloride, $(R)_3SnCl$, $(R)_2SnCl_2$, $RSnCl_3$, carbodiimides, N-cyclic amides, N,N' disubstituted cyclic ureas, cyclic amides, cyclic ureas, isocyanates, Schiff bases, 4,4'-bis(diethylamino) benzophenone, and mixtures thereof wherein R is selected from the group consisting of alkyls having from about 1 to about 20 carbon atoms, cycloalkyls having from about 3 to about 20 carbon atoms, aryls having from about 6 to about 20 carbon atoms and aralkyls having from about 7 to about 20 carbon atoms.

ABSTRACT OF THE DISCLOSURE

A method is presented for anionically polymerizing monomers comprising the step of polymerizing the monomers with a sulfur containing anionic initiator to provide a functional head group on the polymer. Another method provides for anionically polymerizing monomers comprising the steps of synthesizing a sulfur containing anionic initiator *in situ* and polymerizing the monomers with the sulfur containing anionic initiator to provide a functional head group on the polymer. A vulcanizable elastomer having reduced hysteresis properties comprises a plurality of polymer molecules wherein substantially each polymer molecule contains a functional head group derived from a sulfur containing anionic initiator; and from about 20 to about 100 parts by weight of carbon black, per 100 parts of the elastomer. An improved tire having decreased rolling resistance resulting from a treadstock containing a vulcanizable elastomer compound comprises an elastomer comprising a plurality of polymer molecules wherein substantially each polymer molecule contains a functional head group derived from a sulfur containing anionic initiator; and from about 20 to about 100 parts by weight of carbon black, per 100 parts of the elastomer.

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